energy&fuels

UNIVERSITY OF Hull

Subscriber access provided by UNIVERSITY OF HULL

Biofuels and Biomass

Synergistic effects of lignin and cellulose during pyrolysis of agricultural waste.

Roberto Volpe, A. Zabaniotou, and Vasiliki K Skoulou

Energy Fuels, **Just Accepted Manuscript** • DOI: 10.1021/acs.energyfuels.8b00767 • Publication Date (Web): 25 Jun 2018

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Synergistic effects of lignin and cellulose during pyrolysis of agricultural -waste.

Roberto Volpe [1], Anastasia A. Zabaniotou[2] and Vasiliki Skoulou[3,*]

[1] School of Engineering and Material Science, Queen Mary University of London, Mile End Road, London, E1 4NS, U.K.

[2] Department of Chemical Engineering, Aristotle University of Thessaloniki, Un.Box 455, University Campus, GR 541 24, Thessaloniki, Greece.

[3] Chemical Engineering-School of Engineering and Computer Science, University of Hull, HU6 7RX, Kingston Upon Hull, UK.

Abstract. Varying lignin and cellulose contents in agro-waste cause feed-stock to respond differently during their thermochemical conversion. The effect of pyrolysis temperature (400, 500, 600^{o}C) and feedstock composition on product yields and gas composition of Olive-Kernel (OK) and Corn-Cobs (CC) was investigated in a lab-scale, fix bed reactor under a 20mL/min of nitrogen flow at atmospheric pressure. Results were compared to those obtained in the same pyrolysis set up from model synthetic mixtures of cellulose and lignin, in an attempt to simulate the composition of real feedstocks. Experimental results showed how lignin and cellulose influence the thermochemical process and how non-negligible synergistic effects among lignin and cellulose are affecting the thermochemical process outcomes. Lignin affects the increase of char yields obtained from the synthetic mixtures more than it does in real feedstock. Similarly higher yield of CO_2 in produced gas is reported from pyrolysis of synthetic mixtures compared to that obtained from real feedstock containing the same amount of lignin. Thus the pyrolysis behaviour of raw feedstock cannot be

satisfactorily predicted by simulating the behaviour of their main components simply only in an '*additive*' rule, as interactions are also taking place between organic components, as well as ash inorganic elements and organic matter which promote more complex synergistic effects of the components of the lignocellulosic matrix during pyrolysis.

Keywords: Lignin; cellulose; agricultural waste; pyrolysis; product yields; gas composition.

*Corresponding Author: E-mail: v.skoulou@hull.ac.uk (Dr. Vasiliki Skoulou)

Abbreviations:

CC: Corncobs

OK: Olive Kernel

CM: Cellulose microcrystalline

LP: Lignin

1. Introduction

According to the latest World Bioenergy Association (WBA) [1] report 50.5 EJ of bioenergy corresponding to 14% of the global energy mix is consumed globally. A percentage of 7.1% corresponds to the derived heat which is mainly produced in power plants using waste from the forest sector and approximately 28% is directly consumed for direct heat production in residential sector (fireplaces, stoves etc.). Rich in lignin waste accounts for 87% of the total biomass waste supply, while herbaceous waste (agro-waste) emerging from agricultural sector contributes only by a 10% in the field, leaving aside a huge alternative fuel source (World Bioenergy Association (WBA) [1]). Even though waste from the agro-industrial sector can be mainly used as feedstock for the future biorefineries, residues and waste can be used as alternative fuels for bioenergy closing the loop in materials and meeting the sustainability target of bioenergy in a cascade biorefinery scenario [2]. Towards increasing the supply of feedstock from these sectors, various types of lignocellulosic waste can become potential feedstocks for bioenergy generation i.e. via pyrolysis for production of liquid biofuels or by utilizing them directly as solid fuels in the form of pellets.

Upgrading of lignocellulosic waste derived from agricultural, agro-industrial and forestry sectors to fuel grade feedstock requires primarily a thorough understanding of the interactions between their basic building components (lignin, cellulose) and interactions during the first pyrolytic stage of thermochemical conversion processes, such as combustion or gasification: the pyrolysis stage.

Although the role of lignocellulosic waste as feeding material in bioenergy generation and 2nd generation biofuels production is well reported in literature from a large set of different technologies [3–6], such feedstock varying composition and its effect in thermochemically processed waste products' yields is not yet fully

understood as scientific reports are controversial. Some researchers report negligible interactions between lignin and cellulose during pyrolysis of biomass waste [7,8], while others do report significant interactions [9–15]. In particular Wu and co-authors [16] found that the method by which lignin and cellulose were mixed in feedstock mostly influenced the outcome of pyrolysis.

Lignocellulosic waste is a renewable energy source of diverse origin and composition. From a chemical point of view, lignocellulosic waste is always composed of different weight percentages of the three following natural biopolymers: cellulose, hemi-cellulose and lignin accompanied also from other extractives and inorganics (ash). Lignocellulosic waste's physical properties are related to lignin, cellulose and hemicellulose content, in the plant matrix. Herbaceous feedstocks or agricultural residues, such as cotton or sunflower stalks, contain generally high percentages of cellulose/ hemicellulose in comparison to woody biomass, such as forest waste usually rich in lignin. The structure of lignin component is complex and it is responsible for the woody waste's resistance to enzymatic hydrolysis. Cellulose fibers, on the other hand, are embedded in the lignin polysaccharide matrix [5,6,17–20].

Thermochemical processes such as pyrolysis and gasification are only two of the potential routes to valorise lignocellulosic waste as fuels for energy production [4]. Due to however the current lack of fundamental knowledge of the complex set of reactions occurring during thermochemical breakdown of the lignocellulosic matrix, the development of commercial pyrolysis and gasification technological applications needs more insights in the conversion pathways and synergies of biomass waste's main building blocks [21–23,17]. Understanding how composition of feedstock - in terms of its macro-constituents interactions- influences the thermochemical

breakdown of biomass' main components is important in order to understand the complexity and shed light on the development of innovative biomass waste pyro/gasification technologies.

1.1 Agro-waste composition

Woody and herbaceous biomass waste produced excessively in Mediterranean area such as wheat straw, sunflower stalks, sorghum and many others and their cellulose concentration may reach 40-50wt% [3,6-11]. In some species such as cotton ginning residues and tobacco leafs it reaches the impressive percentage of 95-99wt% [24]. Cellulose $(C_6H_{10}O_5)_n$ is a natural polymer (of n~12000) and made from, among else, glucose ($C_6H_{12}O_6$) monomers which polymerize through d-glyosidic bonds [17,18, 19]. Nowadays, almost 95% of the produced cellulose comes from the wood manufacture industry and is consumed by the paper production industry [27]. Hemicellulose is also a linear biopolymer composed of simple sugar molecules, such as xylose and arabinose and others. Its polymerization degree is considerably lower than the cellulose's (n~ 200) and is present in lignocellulosic waste at weight percentages ranging between 25-30%wt. [27,28].

Lignin, on the other hand, is a highly aromatic polymer whose complex structure is not yet fully understood and is highly dependent on the plant matrix [29,30]. Zhou and co-workers [31] described the nature of chemical bonds between lignin-cellulose and hemicelluloses.

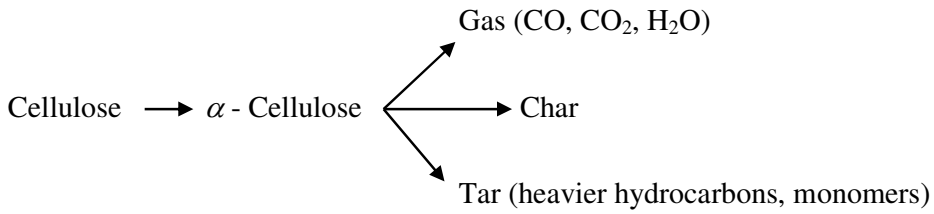
1.2 Thermochemical decomposition of lignin and cellulose

Lignocellulosic biomass waste start to thermally degrade in an inert atmosphere at temperatures above 230^{o}C due to dehydration which results in water (H_2O) molecules

release [32]. Depending on the process conditions of the thermal decomposition, the yields and nature of products may significantly change [19].

Slow pyrolysis takes place under low heating rates (typically between 6 and 60°C/min) and temperatures up to 600°C in an inert environment. Such conditions cause feedstock residence times of 5 to 10 min thereby favoring secondary vapor-solid charring reactions [20, 25-26]. Therefore, solids (pyrolytic chars) are normally the main products (on weight basis) of slow pyrolysis while liquids (heavy condensable hydrocarbons, levoglucosan and aqueous phase) and gases (biomass permanent gases) represent a smaller proportion of the final products [34].

A commonly accepted reaction pathway for cellulose pyrolysis considers a three coupled reactions system of first order towards formation of pyrolytic char, gas, heavy volatile hydrocarbons and monomers (tar), together with the intermediate production of active cellulose (α-Cellulose), as schematically shown in Equation (1) [35]:



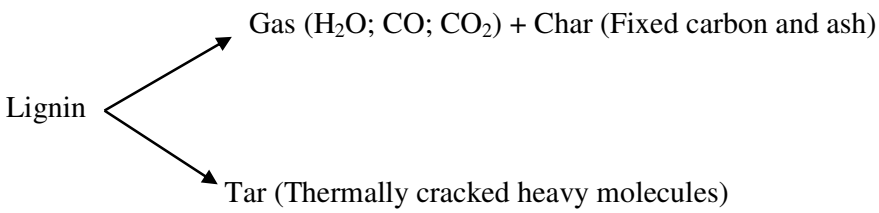
(1)

α-Cellulose is represented as the product of de-polymerization of cellulose towards levoglucosan and lighter molecules. The real nature of α-cellulose and mechanism of production has been object of several studies [36–40]. Levoglucosan is considered a key species during the pyrolytic conversion of lignocellulosic waste yielding from 20 to 60%wt of tar, being either a product or act as an intermediate precursor for the formation of other chemicals during thermochemical decomposition [41].

Several chemical changes such as dehydration, dehydrogenation, decarboxylation and de-oxygenation take place during cellulose pyrolysis. When cellulose is heated in

the temperature range of 200-280°C, a series of endothermic reactions occur and reported earlier by Kilzer and Broido as '*dehydrocellulose*' [32,42]. When slowly heated up to 200°C, cellulose was reported to release mainly H_2O followed by CO and CO_2 when temperature was risen up to 250 °C, meanwhile unsaturated C-C bonds are left in solids [43]. Thus, the intermediate products of cellulose pyrolysis rearrange and lead to generation of new pyrolytic products via condensation and polymerization reactions which release gaseous, tarry and char products.

As for lignin, it's thermal degradation in an inert atmosphere is described via two competitive pathways whereby tarry products or char and gaseous products are formed, with the latter showing a lower activation energy [44]. An equation schematizing lignin pyrolysis is represented below (Equation (2)), [44]:



(2)

During woody waste pyrolysis, lignin starts to dehydrate and deforms at temperatures as low as 130 °C to 190°C, while the maximum rate of decomposition seems to occur between 350-450 °C. Dehydration of lignin requires more intense thermal conditions in comparison to the other macro components while its thermochemical breakdown generates dehydrated products with unsaturated side chains. The broad temperature range in which pyrolysis of lignin takes place appears to relate to the various oxygen (O) functional groups which have different thermal stabilities. The cleavage of such groups leads to the production of gaseous products of low molecular weight (CH_4 and light hydrocarbons). In particular, slow heating rates favour mainly the formation of oxygenated gases such as CO and CO_2, produced generally by the thermal cracking of the carboxyl groups while CH_4 originates from

the breaking of the weak methoxy-groups ($–OCH_3$). H_2 is formed at pyrolysis temperatures above 500°C at the earliest stages of gasification (pyrolytic stages) where inherent H_2O acts also as a gasifying agent, due to the rearrangement and condensation of the structural units of lignin's aromatic rings [44].

The authors described pyrolysis as the first step of gasification process and investigated slow pyrolysis of biomass waste to get insights in possible reaction pathways that occur in the pyrolysis section of a downdraft gasifier [45–47]. In those works chars evolution during thermochemical breakdown and their change in reactivity was affected also by secondary charring reactions.

Gani and Naruse [48], compared thermogravimetric (TG) curves generated during pyrolysis of lignin, cellulose and raw biomass composed of different percentages of lignin and cellulose. Lv and co-workers [49] observed that species containing more cellulose show a thermal decomposition behavior similar of that of pure cellulose while biomasses rich in lignin appear to resemble the depolymerization behavior shown by pure lignin. Regarding synergistic effects among biomass macro-components during thermal breakdown, there has been some contradiction among researches. In general researchers tend to disagree on whether there is any interaction between cellulose and lignin during thermal breakdown of biomass (see for instance different conclusions that authors arrive to in [7] and in [16]), or on whether lignin degrades before cellulose or vice-versa, throughout the different stages of pyrolysis [50,51]. In a recent study, however, George and co-workers, [19] indicated that during fast pyrolysis of mixtures of lignin, xylan (as model compound for hemicellulose) and cellulose in proportions typical of those found in real lignocellulosic biomass precursors, significant synergistic effects are affecting the outcome of the thermal breakdown during fast pyrolysis.

In order to shed additional light on this topic, in the present work, two types of biomass residues, Olive Kernel (OK) rich in lignin and Corn Cobs (CC) rich in cellulose, were pyrolysed in a laboratory scale pyrolysis ring (**Figure 1**). To complement the experiments using the OK and CC agro-residues, synthetic mixtures of pure cellulose microcrystalline (CM) and pure lignin pink (LP) resembling the agro-residues composition, were also pyrolysed in the same set-up. OK and CC have been chosen based not only on their different nature, but also because they are agro-waste which are abundant and create disposal issues in the Mediterranean area during their agricultural production season. Greece as well other Mediterranean countries such as Italy dispose plenty of agricultural and agro industrial waste due to the intensive production of olive oil, corn, cotton and fruits. For this study, olive kernel and corn cob residues emerging from two intensive agro-industrial processes, were selected amongst several existing in Greece and Italy taking into consideration:

a) their availability in Greece, Italy

b) no competition with food -feed industry and

d) their physicochemical properties (density, moisture, C/N ratio) that make them suitable for thermochemical conversion for energy production.

Therefore, the present work helps in evaluating the feasibility of the alternative use of agro-waste which may provide farmers with potentially new routes of income via upgrading and use/sell their waste as alternative feedstock/fuel source for pyrolysis and gasification. In addition, understanding cellulose and lignin behavior during pyrolysis of lignocellulosic biomass is a fundamental step for further studying the thermochemical valorization of other ligno-cellulosic waste [52].

The aim of this study is to investigate the thermal decomposition (slow pyrolysis) of the lignocellulosic waste's macro-molecules by assessing and proving the

synergistic effects among lignin and cellulose constituents and, in turn, to understand if and to what extent it is viable to predict product yields and quality from a known feedstock composition. The main goal of the present study is to further deepen the investigation of slow pyrolysis mechanism, with respect to feedstock macro-constituents and interactions occurring between them. Pyrolysis conditions which may favour optimisation of gas quality will therefore be assessed. By analysing pyrolysis gas products, one may take an elaborated decision as to whether carry out pyrolysis to exploit all product streams or to lead the process further extended into gasification. A comparative analysis then performed on pyrolysis of mixtures of pure lignin and cellulose vs. pyrolysis of raw lignocellulosic materials in present work. The present results may be proved a useful tool to indicate were or to what extent synergies appear among feedstock macro-constituents occurring during thermal breakdown of pyrolysis. Understanding of products yield vs pyrolysis conditions and lignocellulosic waste composition is an important element of knowledge to foster development of sustainable lignocellulosic waste and mixtures thermochemical conversion technologies. The present results would also help developing pyrolysis and or gasification modeling efforts [20]. Identifying then any lignin and cellulose correlations would enable the estimation of the raw lignocellulosics product yields and quality; thus it would be possible to efficiently simulate the pyrolysis and/or gasification processes and derived products and to predict and further proceed with some practical aspects concerning e.g. the selection of the most appropriate feeding materials or mixtures in a biorefinery. In order to compensate with the seasonal production of biomass where the risk between a well-designed or a poor-designed bioenergy system could turn to a loss of profitability over its lifetime and enhance a small biorefinery's competitiveness, simulations are a tool for preliminary estimations.

2. Materials and methods

2.1 Samples preparation and characterization

Olive Kernel (OK) provided by an olive oil production agro-idustry located in an island of the Northern Aegean Sea (Greece), and Conn Cobs (CC) were supplied by a cooperative of farmers, located in the Region of Western Macedonia (Greece), both regions characteristic for their excessive agriculture activity of the agriculture species selected for this study. The samples were dried in open air, chopped, milled and sieved to select samples of particle sizes less than d_p<300μm.

CM and LP were supplied by Sigma Aldrich GmbH and Alfa Aesar U.S.A., respectively. CM appeared as a white microcrystalline powder, while LP appeared as amorphous of dark brown-red colored powder which enabled the visual inspection of through mixing, both samples particle diameters was comprised between d_p=100 and 200μm.

Hosoya and co-workers [13] reported in the past the negligible interactions during the cellulose and hemicellulose pyrolysis up to considerable high temperatures of the range of 800 °C, well above the conventional pyrolysis temperatures. An assumption then was made that the CC and OK agro-residues of interest in this work could be fairly resembled with synthetic mixtures composed only from cellulose and lignin. In addition, as both CC and OK have low hemicellulose content (<20%wt), it was assumed that hemicellulose component might play a secondary, minor role during pyrolysis and the study focused only in the two major components of agro-residues: lignin and cellulose. Then the LP and CM model compounds were thoroughly mixed in weight percentages of 17wt% LP, 83wt% CM (sample named 17LP) and 48wt% LP, 52%wt CM (sample named 48LP) to resemble the behavior of herbaceous CC and

woody OK, respectively. Experiments have also been carried out: 100wt% (pure) CM (sample named 0LP) and 100wt% (pure) LP (sample named 100LP) to serve as a guide of how these pure macromolecules would behave under slow pyrolysis conditions. Ultimate and proximate analysis have been carried out for both raw OK and CC samples in a Thermofinnigan CHNS EA 1112 instrument of CE Instruments and 2960 STD V3.0F thermogravimetric balance using ASTM standards (E-777, E-872). Low heating Value (LHV_b) of raw feedstock was estimated based on the ASTM standard (D-2016-74).

2.4 Pyrolysis experimental study

Experiments were conducted on approximately 1g of samples in the laboratory-scale fixed bed reactor (**Figure 1**) at atmospheric pressure, under of 20mL/min of nitrogen flow corresponding to an approximately 0.4 s of gas residence time in the system. N_2 was preheated upon entering the heated reactor body, while temperature was measured with a K-type thermocouple placed into the reactor's core and was in contact with the fixed bed material. The temperature of the reactor was controlled by means of an electrical furnace set by a Proportional-Integral-Derivative (PID) controller. A pyrolysis gas cleaning, sampling and measurement section completed the experimental rig.

The samples containing respectively 0, 17, 48 and 100 wt % of LP, placed manually in the bottom of the stainless steel reactor, and were pyrolysed by placing the reactor at the core of a furnace pre-heated to the desired temperatures of T=400^{o}C, 500^{o}C and 600^{o}C for pyrolysis to be achieved. Pyrolysis heating rate for all samples was calculated to be approximately 150^{o}C/min.

Temperature data and total gas flow where measured as pyrolysis occurred and experiments would be considered terminated when, after the samples would reach the peak temperature, no more pyrolysis gas was produced and the total flow of gas would coincide with initial flow of the N_2 sweep gas. The time for that to occur was calculated to be approximately 30min for all of the runs. Once the pyrolysis reaction was completed, the lab scale reactor let to cool down to room temperature. At the end of each run, the reactor system was disassemble the char manually collected and weighted to the nearest 0.001 g. The produced pyrolysis gas yields were calculated in volume and weight in a normalized N_2 free basis. The total tar yield, including aqueous phase and intermediate liquid products, was determined by difference.

Prior to sampling, produced gas was conditioned by means of two bubblers placed one after the other, the first being filled with deionized water and second with isopropanol. The tar trap was also followed by a fiber glass-silica gel filter fitted at end of the gas cleaning-sampling line and the latter was placed to absorb any remaining moisture. Both bubblers were immersed in an ice/salt cooling bath kept at approximately -1°C.The produced gas was then sampled in air tight bags and led to offline analysis in a Model 6890N, Agilent Technologies gas chromatograph fitted with two columns, HP-PlotQ and HP-Molsieve type and two detectors a FID and TCD. To complete the analysis the pyrolysis gas composition and product yields from pyrolysis of raw OK and CC at 600^{o}C under the same set-up conditions were also determined. **Table 1** tabulates the process conditions of the experiments carried out, while repeatability of experimental results tested as experiments carried out three times and found that the experimental error was within the acceptable ranges of <10% and the mean value is presented in figures.

3. Results and Discussion

3.1 Proximate and ultimate analyses of OK and CC

Proximate and ultimate analyses of OK and CC was performed and the results are presented in **Table 2** Those data support the initial assumption that both OK and CC are suitable for further exploitation by thermochemical processes. In particular, samples had moisture content lower than 50wt%, adequate low heating value (LHV_b) and a C/N molar ratio over 30 which all the above information indicate that the thermochemical valorization route towards value added solid fuel would be an attractive option. Moreover, the ultimate analysis, validated the assumption that the CC is categorized as herbaceous (~$CH_{1.6}O_{0.8}$) and that OK may be categorized as woody biomass (~$CH_{1.2}O_{0.4}$) according to classification reported by Fryda [53]. It may also be noted that although S content appears relatively high in the LP sample when estimated on weight basis and based on the molecular formula, sulfur is expected to be negligible in the LP sample and for the weights and weight percentages used in this work.

3.2 Pyrolysis of pure cellulose and lignin and their model synthetic mixtures

3.2.1 Pyrolysis product yields

In **Figure 2** the gas, char and tar product yields (wt%) from pyrolysis of all samples are reported. Results indicate that irrespectively to pyrolysis temperature, the higher the lignin content in sample is, the higher the char yield is. This aligns with the fact that higher lignin content, which means higher aromaticity and therefore all else being unvaried, more energy is needed to break down the stronger aromatic bonds in

solids [46]. In addition it may be observed that the higher the lignin content is in both samples and mixtures, the less sensitive to pyrolysis temperature the char yield is.

Experimental results shown in **Figure 2** show how the pure lignin sample yields approximately 50 wt% d.b. of char at all three temperatures tested (400, 500, 600^{o}C). In the case of the pure cellulose sample (0LP) it produces as expected a significantly lower amount of char yield (maximum ~22 wt% d.b. at 400^{o}C). The latter however is more sensitive to pyrolysis temperature, than the char produced from pure lignin pyrolysis. In fact, the char yield produced from pure cellulose, and between 400°C - 600°C, decreased by more than half from 22 wt% to approximately 9 wt%, respectively. The high char yield in samples containing higher amounts of lignin, may be also related to the rearrangement of the lignin aromatic structure with temperature. Brebu and Vasile [44] reported that the cleavage of the aryl-ether bonds in lignin results in formation of a very active but yet unstable free radicals rearranging further to form products of higher stability, such as char.

Tar yields, on the other hand, are generally higher for the higher cellulose content samples, while not clear conclusive data may be reported with respect to the sensitivity of tar yield to pyrolysis temperature. This might be attributed to hemicellulose which might have different thermal behaviour resulting in both different product yields and gas, liquids composition but was not a subject of this study. In general, and as also reported by Lv and co-workers [49], for the temperature range under consideration, cellulose tends to produce higher condensable volatile (or tar) yields, while lignin contributes mainly to the increased char yield. The char yield is also directly depended on secondary vapour-solids reaction [36,45,46,54,55]. These reactions are responsible for more char formation related to tar cracking on hot char particles. With this respect, the present results allow concluding that some effect of

secondary reactions may be evident on lower lignin content samples and appear to have little influence on higher lignin content samples. This may be due to the higher aromaticity and stability of lignin portion in sample. Hence, tar would crack on solid chars more significantly if solid particles would be more subject to chemical interaction with char. Hosoya and co-workers [12] had also observed that the presence of lignin inhibits the thermal polymerization of levoglucosan, a primary product of cellulose pyrolysis, with increasing temperature.

The present also of Ca^{++} and Na^{+} cations, characteristic of wood lignin, in the LP sample and OK as shown in **Table 3**, was in fact expected to increase with increase of lignin (LP) content in synthetic mixtures i.e. have a more prominent effect to charring reactions in woody than in herbaceous waste tested as also noticed by Brebu and Vasile [44].

In the samples of the lower lignin content, on the other hand, the higher presence of cellulose may have reduced char yield by promoting char decomposition, this may be explained considering that cellulosic chars are expected to be more reactive during thermochemical treatments than lignin ones. This is also observed by the consistently lower tar yields in higher lignin content samples for all the temperatures analyzed. Additionally, the presence of lignin seemed to inhibit the formation of intermediates (tar precursors) during pyrolysis of mixtures at 500 and 600 °C, indicating that tar precursors are originated mainly from cellulose. The presence of lignin tend to stabilize the evolving radicals on solid matrix. The aromatic structure of lignin promotes stabilization, while less aromaticity promotes more tar forming reactions.

Antal and Vareghyi [36], Dabai at al, [56] and Volpe at al. [45,46] observed that the vapour-solids interaction leads to more intensive char formation, too. Sadaka and co-workers [57], had also earlier observed that low pyrolysis temperatures lead to

char production followed by the release of moisture. Then, when temperature increases, more tar is converted to gaseous species and this is favoured in slow rate pyrolysis set-ups where tarry components have sufficient time to undergo thermal cracking. In addition, smaller particle sizes and low moisture content are both reported to favour tar production [58].

3.2.2 Gas composition

Figure 3 depicts the gas composition of the four synthetic feedstocks analyzed in the present study. Data show a systematic increase in CO_2 production with increasing the presence of lignin at 500 and 600 °C pyrolysis attempts with the highest proportion of CO_2 being released from the pure lignin sample.

Pyrolysis of lignin, is known to occur more gradually over a wide range of temperatures compared to cellulose [36]. Thermal breakdown of lignin starts with the cleavage of the weaker molecular bonds at the lower temperatures, to progress with the breaking of the aromatic rings and the release of hydrogen at temperatures above 500 °C [59]. Accordingly, in our experiments, from 400 °C to 600 °C, pyrolysis of pure lignin resulted in a largely stable and relatively high CO_2 concentration in the produced gas. On the other hand, a significant reduction in CO which passed from 16% vol to 5 %vol was noticed with increasing temperature, while H_2 was detected in low concentrations only at the highest temperature (600 °C). Lighter hydrocarbons (C_2H_x) and methane (CH_4) were released in traces only at the highest 600 °C temperature.

By ignoring the low amounts of CH_4 and other light hydrocarbons, a clear difference between pure cellulose and samples containing lignin can be noticed. Whatever the tested temperature, pure lignin samples appear to release a significantly

higher amount of CO_2 and lower amount of CO compared to samples containing cellulose. Moreover the higher the lignin content, above 17%wt d.b., the higher the release of CO_2 and lower the release of CO is. In both samples of pure cellulose and pure lignin, the largest changes in gas composition occur between 400 and 500 °C, while no considerable changes appear thereafter between 500 and 600 °C. In particular, a temperature increase from 400 to 500 °C during cellulose pyrolysis, causes an approximately 10%vol reduction of CO_2 and lower 5% vol changes in CO concentration. Moreover, pure lignin shows an increase of about 10% vol in CO_2 concentration and a significant decrease of approximately 10% vol in CO concentration, between 400 and 500 °C. When temperature is further increased to 600 °C, CO in pure lignin is further reduced to a value of about 5%vol in concentration, approximately a quarter of the initial value. Considerably high concentrations of CO_2, when compared to other gases, were also found for all feedstocks. According to previous works [52], CO_2 release is linked to the primary reactions of early pyrolysis stages of cellulose. Also, CO_2 and CO release in relatively high proportions, in samples containing cellulose, is a probable indication of the exothermic reactions responsible for char production due to secondary vapour-solids interactions occurring favoured by the presence of cellulose as discussed. This was also reported earlier by Mok and Antal [60]. Cellulose pyrolysis is also known [32] to proceed via intermediate stages of levoglucosan dehydration towards char and low molecular weight products (among which primarily CO_2, H_2O, furan, acids etc.).

Data from the present work show also that pyrolysis of cellulose leads to release of more H_2 at temperatures ~400 ^oC, possibly due to cracking of the cellulose's macromolecules. On the other hand, CH_4 concentration hardly reached 4%vol in the gaseous mixture even at the highest tested temperature (600 ^oC). As reported by

Houben and colleagues [61], methane might be formed by hydrogenation of one of the double bonds of an aromatic ring which in this case would occur in cellulose chars at higher temperatures, while we would expect the formation of aromatic structures due to reorganization of solid matrix [46]. The same mechanism was earlier suggested by Howard [62] for the pyrolysis of coal and years later also by Nelson and Huttinger [63] regarding the hydropyrolysis of naphtalene and other aromatics used as model compounds for tar. Particularly evident with this respect appears what is shown for pure cellulose sample at 500 and 600 °C. The relative large amount of 19.2 %vol of H_2 released during pyrolysis at 500 °C appears to be significantly reduced to approximately 5.8% vol at 600 °C. Correspondingly, the traces of CH_4 are hardly detectable during pyrolysis at 500 °C while increase to as much as 4.4% vol at 600 °C.

The increasing presence of lignin in samples seems to decrease the phenomenon at lower temperature so that thermal decomposition of lignin seems not to favour the H_2 release until 600 °C. CH_4 and other lighter hydrocarbons (C_2H_x) disappear as the temperature increases.

Results seem to show that the long residence time during pyrolysis, might have favoured the promotion of the water gas shift (WGS) and adverse Boudouard reactions following Eq. (3) and (4) responsible for H_2 and CO_2 release, in cellulose samples at the lower tested temperatures and lignin containing samples at the higher temperatures.

$$CO+H_2O=>CO_2+H_2 \quad (3)$$

$$2CO=>C+CO_2 \quad (4)$$

The presence of water (H_2O) molecules released by cellulose and lignin pyrolysis seemed to further facilitate the early gasification of lignin resulting in the CO_2 concentration increase at the highest temperature (600^oC) [64].

3.2.3 Comparison between raw lignocellulosic waste and synthetic mixtures

Experimental results depicted in **Figure 4** show that pyrolysis of real OK resulted in a 15% higher char and 69% higher gas yields, while tar yield results 21% lower compared to CC waste.

This was probably due to a number of reasons. Firstly the fact that CC agro-waste has naturally considerably high cellulose content and higher moisture content in lignin may have favored the production of char in an environment where vapors experience contact with char-solids before escaping the reaction zone. Moisture, in fact, is known to auto-catalyze char forming reactions [36]. Secondly, the higher lignin content of the woody waste of OK, at a relatively low temperature may have facilitated both further polymerization and heavier hydrocarbons (tar precursors) reforming over char followed by coke (C) deposition [65]. The relatively high reactivity of OK char in comparison to chars from other biomass species, as well as the self-catalytic effect of inorganic species of ash in feedstock **(Table 3)** is also reported in literature [66,67] and the naturally inherent ash in raw samples played a role towards this. Additionally the more thermally stable lignin in woody biomass such as in OK is reported to produce more char than that in herbaceous biomass [44]. This trend could be also associated with the increase of CH_4 and C_2H_X concentration in gas produced during OK pyrolysis shown in **Figure 5**.

Both woody (OK) and herbaceous (CC) lignocellulosic waste produced a pyrolysis gas of relatively high CO_2 concentration, followed by CO. In particular, OK pyrolysis gas showed 30.9% (%vol) more H_2 than CC, while CO_2 concentration resulted

approximately 6.5% higher. On the other hand, CO concentration in OK pyrolysis gas resulted 54.9% lower in comparison to CC. At the same time 48% more ethane (C_2H_6) and ethylene (C_2H_4), as well as, a 62.6% more methane (CH_4) produced when OK pyrolyzed instead of CC.

The higher initial moisture content in OK, as well as the water released during the first steps of pyrolysis, might have facilitated the breakdown and degradation of the pyrolysis intermediate molecules. Additionally, long residence time related to slow heating rate of the experimental system, in combination with a relatively high pyrolysis temperature (600 ^{o}C) may have also promoted the water gas shift reaction towards an increase in H_2 and CO_2 concentration in pyrolysis gas. In addition the low concentration of light hydrocarbons (C_2H_X<5%vol) detected in pyrolysis gas phase, aligns with what was found on previous studies by Sadaka and co-workers [57].

Figure 6 presents the product yields (%wt d.b.) during pyrolysis of CC and OK at 600^{o}C compared to products of thermal breakdown of synthetic lignocellulosic mixtures, which carry the same lignin content and possible predictions based on the additive rule. Results show some differences occurring between real and synthetic mixtures for both feedstocks under analysis. Synergistic effects between the lignin and cellulose during pyrolysis of the real and artificial mixtures may be inferred, and as shown in **Figure 6** cannot be predicted by simply applying the additive rule**.**

It can be seen from **Figure 6** in particular that low lignin content with high cellulose artificial mix and real CC feedstock, present measurably different tar and gas yields and similar char yield. On the contrary, higher lignin content feedstocks such as OK and artificial mixture present substantially similar char and gas yields and significant differences in tar yields. In both low and high lignin content materials, therefore, lignocellulose macro constituent play a different role as they are embedded

in parent matrix rather than joined in an artificial mixture. Cellulose in real feedstock is responsible for higher formation of precursors which appear to be able to more easily coalesce and thus be released as tarry vapours. On the other hand, in the synthetic mixtures, tar precursors more easily crack on the lignin in mixture to produce more gas. Higher gas yield produced in OK, compared to the 48LP synthetic mixture, may be related to higher ash content in real feedstock and their catalytic effect in tar cracking [68].

Deviations in the experimental data and more complex synergies between real feedstock and synthetic mixtures also concern the composition of the gas released, as it can be noticed from **Figure 7**. A measurable difference between CO_2 and CO yields in the low lignin content samples shows a yield in a more oxidized gas for the real sample compared to the synthetic mixture. This may be related to the oxidizing effect that levoglucosan has during pyrolysis of biomass with relatively high cellulose content [19]. The higher lignin content samples 48LP and OK, show a remarkably similar yield in CO_2, however, lower CO yield in real feedstock favoured higher yield of hydrogen, CH_4 and light hydrocarbons. This appears related to the lower char yield measured in real sample vs synthetic mixture and the early gasification of chars at 600 °C possibly favoured by the higher moisture content. In general, the higher yields in hydrogen, methane and light hydrocarbons, reported in both real samples compared to the synthetic mixtures may be related to the catalytic effect of the parent biomass ash constituents and their catalytic effect during the thermal treatments [19,50] which also plays a major role during the pyrolysis process.

At 600 ^{o}C, pyrolysis of CC led to the production of less CO_2 and H_2 amounts and more CO and tar compared to its synthetic mixture. This behaviour could be related to the initial CC moisture content which might have favoured some preliminary

gasification reactions at that temperature level. The relatively slow heating rate and the reactions between vapours and solids might also have caused an increase in secondary charring [45], while ash content in real feedstock might have favoured cracking of tar precursors.

Raw OK produced a pyrolysis gas with lower CO and similar CO_2 and higher H_2 and CH_4 concentrations in comparison to the synthetic mixture prepared by lignin and cellulose. The reason was the moisture content of the raw material, as well as the known increased reactivity of the OK char towards gasification products and syngas. Again the histograms representing the additive law in **Figure 7** indicate that synergies exist.

Taking into consideration all the above results, by applying the additive law revealed, significant deviations between the experimental data concerning the gas product yield of the raw lignocellulosic residues in comparison to their synthetic mixtures was observed. This implies that not only gas-gas reactions take place but also gas-solid reactions and catalytic effect of biomass ash probably occurs. Thus, although synergetic effects of the main building blocks of lignocellulosics are evident, the additive law cannot be applied.

3 Conclusions

Pure cellulose (CM), lignin (LP) and their model synthetic mixtures simulating a woody and a herbaceous lignocellulosic wastes were pyrolyzed in a lab scale fixed bed reactor at slow heating rate to evaluate effect of pyrolysis temperature (T=400-600 ^{o}C) on the product yields and composition of the produced gas.

The results showed:

- The effect of lignin in the pyrolysed mixtures: increasing char yields and reducing tar yields at all the tested pyrolysis temperature.
- Lignin in synthetic mixtures is responsible for increased CO_2 in the produced gas.
- The presence of lignin has also shown to inhibit the production of H_2 in the gas; this, though was not found in real feedstock containing the same amount of lignin.
- Significant more hydrogen and methane in OK sample, at 600°C is related to a possible early gasification of raw feedstock's char due to higher moisture content and also to a probable catalytic effect of ashes in the raw feedstock's matrix.
- Experimental results showed that the behaviour of real lignocellulosic waste during pyrolysis may not be predicted only by the '*additive rule'* (simply adding results obtained from pyrolysis of the lignocellulosic macro-constituents of lignin and cellulose) which however seems to resemble better woody biomass than herbaceous biomass waste. In addition the self catalytic effect of inherent ash in raw feedstock changed considerably the interactions towards gaseous, solid and tarry products during slow pyrolysis conditions.
- They also provided a good insight in the pathways that lead to the production of hydrogen in samples which contain lignin and H_2 is produced at higher temperature and concentration in real feedstock compared to the model synthetic mixture.

Acknowledgements

Dr V. Skoulou is grateful to the State Scholarships Foundation (I.K.Y) (Contract No: 950; 2010/11) for funding part of the present work. Special thanks are also devoted to Assoc. Prof. G. Stavropoulos for his in kind support by providing both chemicals and the experimental rig.

References

[1] B. Kummamuru, No Title, WBA Glob. Bioenergy Stat. 2017. (2017).

[2] Zabaniotou, A. ;Kamaterou, P.; Kachrimanidou, V.; Vlysidis, A.; Koutinas, A., , J. Clean. Prod. **2017**, 172, 4119-4129 doi:10.1016/j.jclepro.2017.01.151.

[3] Sanders, J. ; van der Hoeven, D. Energies. **2008,** *1* , 105–119. doi:10.3390/en1030105.

[4] Basu, P.Biomass gasification and pyrolysis : practical design and theory, Academic Press, 2010.

[5] Titirici, M.-M. ; Funke, A.; Kruse, A.Thermochemical conversion of biomass, in: Recent Adv. Thermochem. Convers. Biomass, Elsevier, 2015.

[6] Ronsse, F.; Nachenius, R.W.; Prins, W.Carbonization of Biomass, Elsevier B.V., 2015. doi:10.1016/B978-0-444-63289-0.00011-9.

[7] Hilbers, T.J.; Wang, Z. ; Pecha, B.; Westerhof, R.J.M.; Kersten, S.R.A.; Pelaez-Samaniego, M.R.; Garcia-Perez, M. J. Anal. Appl. Pyrolysis **2015** , *114*, 197–207. doi:10.1016/j.jaap.2015.05.020.

[8] Zhang, J.; Choi, Y.S. ; Yoo, C.G.; Kim, T.H.; Brown, R.C.; Shanks, B.H., ACS Sustain. Chem. Eng. **2015,** *3*, 293–301. doi:10.1021/sc500664h.

[9] Giudicianni, P.; Cardone, G.; Ragucci, R., J. Anal. Appl. Pyrolysis **2013,** *100*, 213–222. doi:10.1016/j.jaap.2012.12.026.

[10] Giudicianni, P. ; Cardone, G. ; Sorrentino, G. ; Ragucci, R. J. Anal. Appl. Pyrolysis **2014**, *110*, 138–146. doi:10.1016/j.jaap.2014.08.014.

[11] Gargiulo, V.; Giudicianni, P. ; Alfè, M.; Ragucci, R. x, J. Anal. Appl. Pyrolysis **2015**, *112*, 244–252. doi:10.1016/j.jaap.2015.01.018.

[12] Hosoya, T. ; Kawamoto, H.; Saka, S. Carbohydr. Res. **2006** , *341*,2293–2297. doi:10.1016/j.carres.2006.06.014.

[13] Hosoya, T. ; Kawamoto, H. ; Saka, S. J. Anal. Appl. Pyrolysis **2007**, *80*, 118–125. doi:10.1016/j.jaap.2007.01.006.

[14] Liu, Q.; Zhong, Z. ; Wang, S. ; Luo, Z. J. Anal. Appl. Pyrolysis **2011**, *90,* 213–218. doi:10.1016/j.jaap.2010.12.009.

[15] Wang, S.; Guo, X. ; Wang, K.; Luo, Z. J. Anal. Appl. Pyrolysis. **2011**, *91*, 183–189. doi:10.1016/j.jaap.2011.02.006.

[16] Wu, S.; Shen, D.; Hu, J.; Zhang, H.; Xiao, R.C Biomass Bioenergy **2009**, *90*,209–217. doi:10.1016/j.biombioe.2016.04.012.

[17] Demirhan, H.; AZ, I.F.; Skoulou, V. ; Haywood, S.; Zein, S. Curr. Microw. Chem. **2017**, *4* (3), 2005-2018.

[18] Di Blasi, C.; Branca, C. ; Sarnataro, F.E.; Gallo, A., Energy and Fuels. **2014** , *28* , 2684–2696. doi:10.1021/ef500296g.

[19] George, A.; Morgan, T.J. ; Kandiyoti, R. , Energy & Fuels **2014**, *28*, 6918–6927. doi:10.1021/ef501459c.

[20] Di Blasi, C.; Branca, C. ; Galgano, A., Energy Technol.**2017** , *5* ,19–29. doi:10.1002/ente.201600091.

[21] Simoneit, B.R.T. ; Schauer, J.J.; Nolte, C.G.; Oros, D.R.; Elias, V.O.; Fraser, M.P.; Rogge, W.F.; Cass, G.R. Atmos. Environ. **1999**, *33*,173–182.

[22] Boonmee, N.Theoretical and experimental study of autoignition of wood, PhD Thesis, University of Maryland, 2004.

[23] Mettler, M.S.; Vlachos, D.G.; Dauenhauer, P.J. Energy Environ. Sci. **2012**, 57797. doi:10.1039/c2ee21679e.

[24] Data Base for Biomass and Waste, 2017. https://www.ecn.nl/phyllis2/.

[25] Updegraff, D.M. Anal. Biochem. **1969**, *32*, 420–424. doi:10.1016/S0003-2697(69)80009-6.

[26] Bidlack, J.; Malone, M.; Benson, R. Molecular Structure and Component Integration of Secondary Cell Walls in Plants, in: Proc. Okla. Acad. Sci, 1992; pp. 51–56.

[27] Clark, J.H.; Deswarte, F.E.I.Introduction to chemicals from biomass, Wiley, 2015.

[28] Mohan, D. ; Pittman, C.U.; Steele, P.H. Energy & Fuels. **2006**, *20*, 848–889. doi:10.1021/ef0502397.

[29] Sjotrom, E. Chapter 4 – LIGNIN, in: Wood Chem., 1993: pp. 71–89. doi:10.1016/B978-0-08-092589-9.50008-5.

[30] Chen, Z.; Wan, C.Biological valorization strategies for converting lignin into fuels and chemicals, Renew. Sustain. Energy Rev. **2017**, *73*, 610-621. doi:10.1016/j.rser.2017.01.166.

[31] Zhou, Y.; Stuart-Williams, H. ; Farquhar, G.D.; Hocart, C.H. Phytochemistry **2010**, *71*, () 982–993.

[32] Kilzer, F.J.; Broido, A. Pyrodynamic. **1965** , *2* , 151–163.

[33] Bridgwater, A. V. Wiley InterScience (Online service), Progress in thermochemical biomass conversion, Blackwell Science, 2001.

[34] Goyal, H.B.; Seal, D.; Saxena, R.C. Bio-fuels from thermochemical conversion

of renewable resources: A review Renew. Sustain. Energy Rev. 2008, *12* (2), 504–517. doi:10.1016/j.rser.2006.07.014.

[35] Broido, A.Kinetics of Solid-Phase Cellulose Pyrolysis, in: F. Shafizadeh, K. V. Sarkanen, D.A. Tillman (Eds.), Therm. Uses Prop. Carbohydrates Lignins, Academic Press: New York, 1976: pp. 19–35.

[36] Antal, M.J.J.; Varhegyi, G. Ind. Eng. Chem. Res. **1995**, *34*, 703–717. doi:10.1021/ie00042a001.

[37] Ali, M.; Apperley, D.C. ; Eley, C.D.; Emsley, A.M.; Harris, R.K. Cellulose. 1996, *3*, () 77–90. doi:10.1007/BF02228792.

[38] Emsley, A.M.; Stevens, G.C. Cellulose. **1994**, *1* , 26–56. doi:10.1007/BF00818797.

[39] Zhu, G.; Zhu, X.; Xiao, Z.; Yi, F. J. Anal. Appl. Pyrolysis. **2012**, *94* ,126–130. doi:10.1016/j.jaap.2011.11.016.

[40] Shen, D.; Xiao, R.; Gu, S.; Zhang, H.The Overview of Thermal Decomposition of Cellulose in Lignocellulosic Biomass, in: Cellul. - Biomass Convers., InTech, 2013. doi:10.5772/51883.

[41] Zhang, X.; Yang, W.; Blasiak, W. J. Anal. Appl. Pyrolysis. **2012**, *96*, 110–119. doi:10.1016/j.jaap.2012.03.012.

[42] Arseneau, D.F. Can. J. Chem. **1971**, *49* , 632–638. doi:10.1139/v71-101.

[43] Pastorova, I;. ; Botto,R.E.; P. ; Arisz, P.W.; Boon, J.J. Carbohydr. Res. **1994**, *262* (1), 27-47. ().

[44] Brebu, M.; Vasile, C. Cellul. Chem. Technol. **2010,** *44* ,353–363.

[45] Volpe, R. ; Messineo, A.; Millan, M. Fuel. **2016**, *183* ,139–144. doi:10.1016/j.fuel.2016.06.044.

[46] Volpe, R.; Menendez, J.M.B.; Reina, T.R.; Messineo, A.; Millan, M. Fuel Process. Technol. **2017**, *158* ,255–263. doi:10.1016/j.fuproc.2017.01.015.

[47] Skoulou, V. ; Zabaniotou, A. Catal. Today. **2012**, *196* , 56–66. doi:10.1016/j.cattod.2012.03.035.

[48] Gani, A., Naruse, I., Renew. Energy. **2007**, *32* , 649–661. doi:10.1016/j.renene.2006.02.017.

[49] Lv, D. ; Xu, M.; Liu, X. ; Zhan, Z.; Li, Z.; Yao, H. Fuel Process. Technol. **2010**, *91*, 903–909. doi:10.1016/j.fuproc.2009.09.014.

[50] Couhert, C.; Commandre, J.-M.; Salvador, S. Fuel. **2008,** *88* 408–417. doi:10.1016/j.fuel.2008.09.019.

[51] Yang, H. ; Yan, R.; Chen, H.; Zheng, C. ; Lee, D.H.; Liang, D.T. Energy &

Fuels **2006**, *20* , 388–393. doi:10.1021/ef0580117.

[52] Shen, D.K.; Gu S., Bioresour. Technol. **2009**; *100*, 6496–6504. doi:10.1016/j.biortech.2009.06.095.

[53] Fryda, L. Development of advanced power production systems with biomass utilization, PhD thesis, National Technical University of Athens, 2006.

[54] Antal, J. M. J.; Grønli, M.I*nd. Eng. Chem. Res.*, **2003**, *42* (8), 1619–1640 doi:10.1021/IE0207919.

[55] Morgan, T.J.; Kandiyoti, R. Chem. Rev. **2014**, *114*, 1547–1607. doi:10.1021/cr400194p.

[56] Dabai, F.; Paterson, N.; Millan, M.; Fennell, P.; Kandiyoti, R. Energy & Fuels. **2014**, *28*, 1970–1982. doi:10.1021/ef402293m.

[57] Sadakata, M. ; Takahashi, K. ; Saito, M.; Sakai, T. Fuel. **1987**, *66* , 1667–1671. doi:10.1016/0016-2361(87)90360-7.

[58] Zabaniotou, A.A.; Kalogiannis, G. ; Kappas, E.; Karabelas, A.J. Biomass & Bioenergy. **2000**, *18* , 411–420.

[59] Pandey, M.P.; Kim, C.S. Chem. Eng. Technol. **2011,** *34* ,29–41. doi:10.1002/ceat.201000270.

[60] Mok, W.S.-L.; Antal, M.J. Thermochimal Acta. **1983**, *68* 155–164.

[61] Houben, M.P.; De Lange, H.C.; Van Steenhoven, A.A. Tar reduction through partial combustion of fuel gas, Fuel **2005** , *84* (7-8), 817-824. doi:10.1016/j.fuel.2004.12.013.

[62] Howard, J. Fundamentals of coal pyrolysis and hydropyrolysis, in: M. Elliot (Ed.), Chem. Coal Util., John Wiley and Sons, Inc., New York, 1981: pp. 665–784.

[63] Nelson, P.F.; Hüttinger, K.J. Fuel. **1986**, **65** , 354–361. doi:10.1016/0016-2361(86)90295-4.

[64] Kumar, P.; Barrett, D.M.; Delwiche, M.J.; Stroeve, P. Ind. Eng. Chem. Res. **2009** , 48 , 3713–3729. doi:10.1021/ie801542g.

[65] Hosokai, S.; Norinaga, K.; Kimura, T. ; Nakano, M.; -Z. Li, C.; Hayashi, J. Energy & Fuels. **2011,** *25* , 5387–5393. doi:10.1021/ef2003766.

[66] Skoulou, V. ; Swiderski, A.; Yang, W. ; Zabaniotou, A. Bioresour. Technol. **2008**, 100 ,2444–2451. doi:10.1016/j.biortech.2008.11.021.

[67] Zanzi, R.; Sjostrom, K. ; Bjornborn, E. Biomass & Bioenergy. **2002** , 23, 357–366.

[68] Huyghe, J.The role of alkali and earth alkaline metals as intrinsic catalysts in

the fast pyrolysis of biomass constituents, University Gent, 2013.

Figures

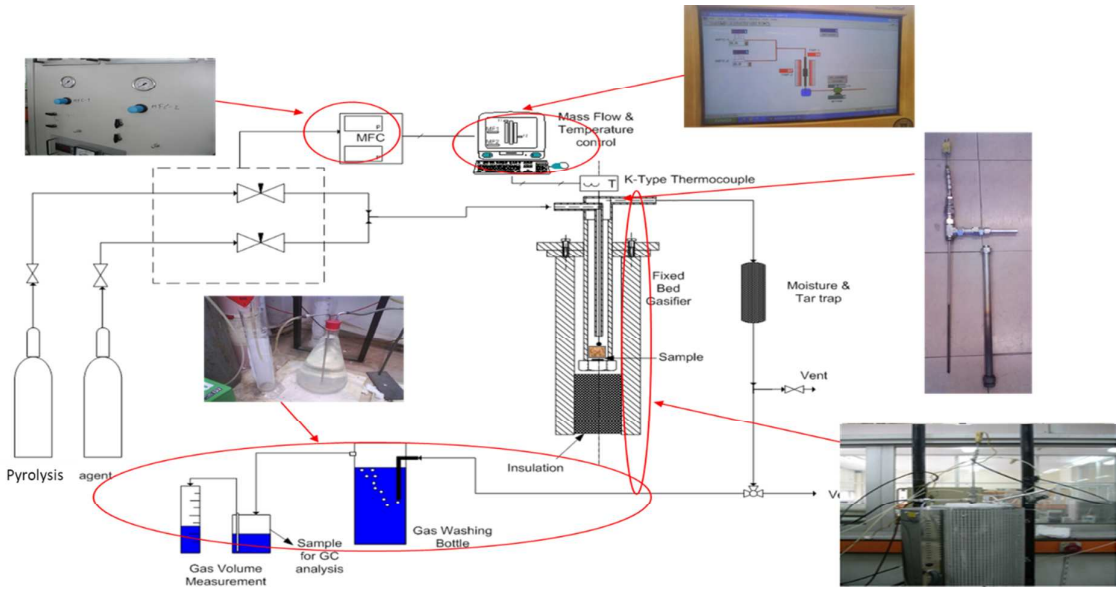
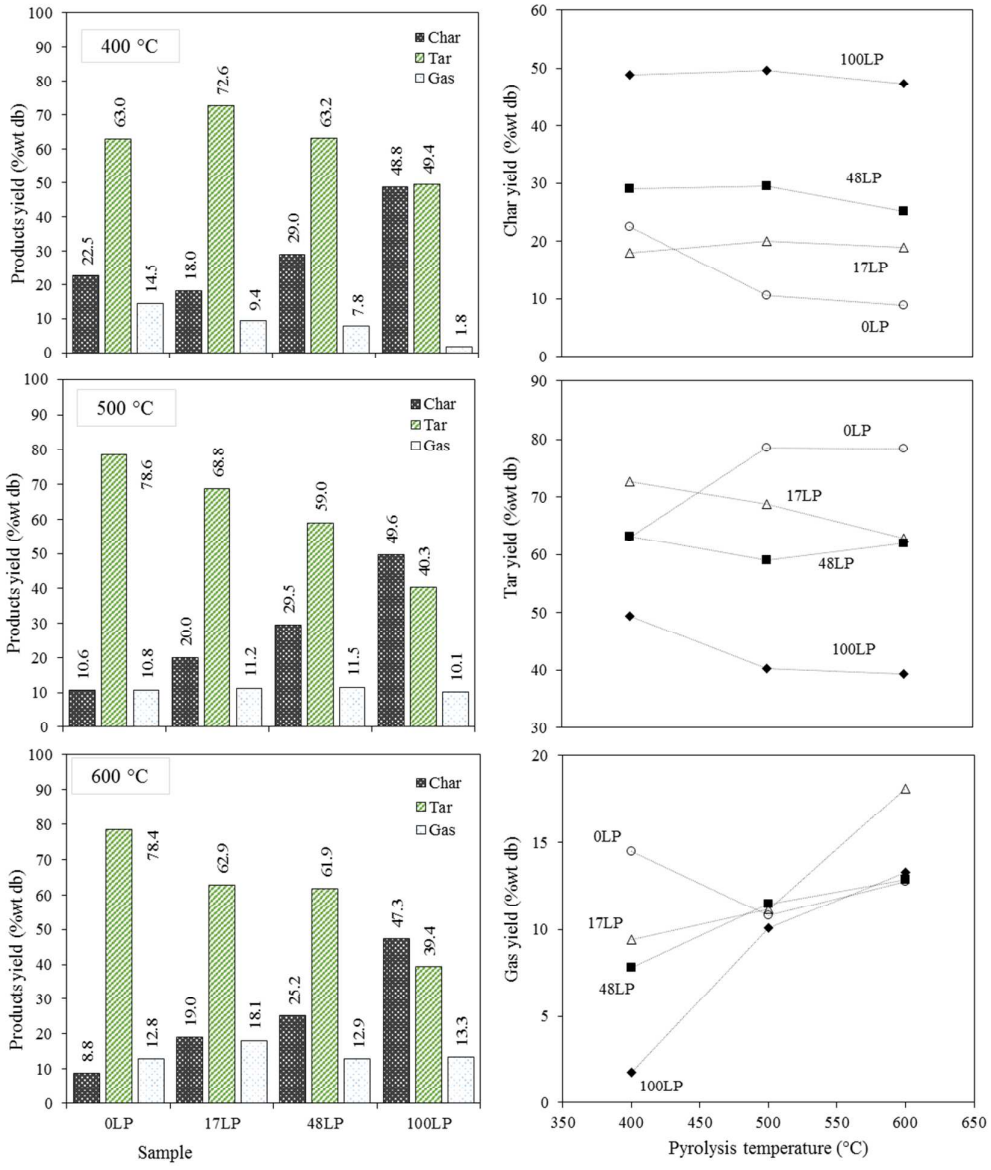


Figure 1 Lab scale fixed bed agro-waste pyrolysis rig.



744

745 **Figure 2** Products yield (%wt, d.b.) of different lignin-cellulose model mixtures

746 versus pyrolysis temperature.

747

748

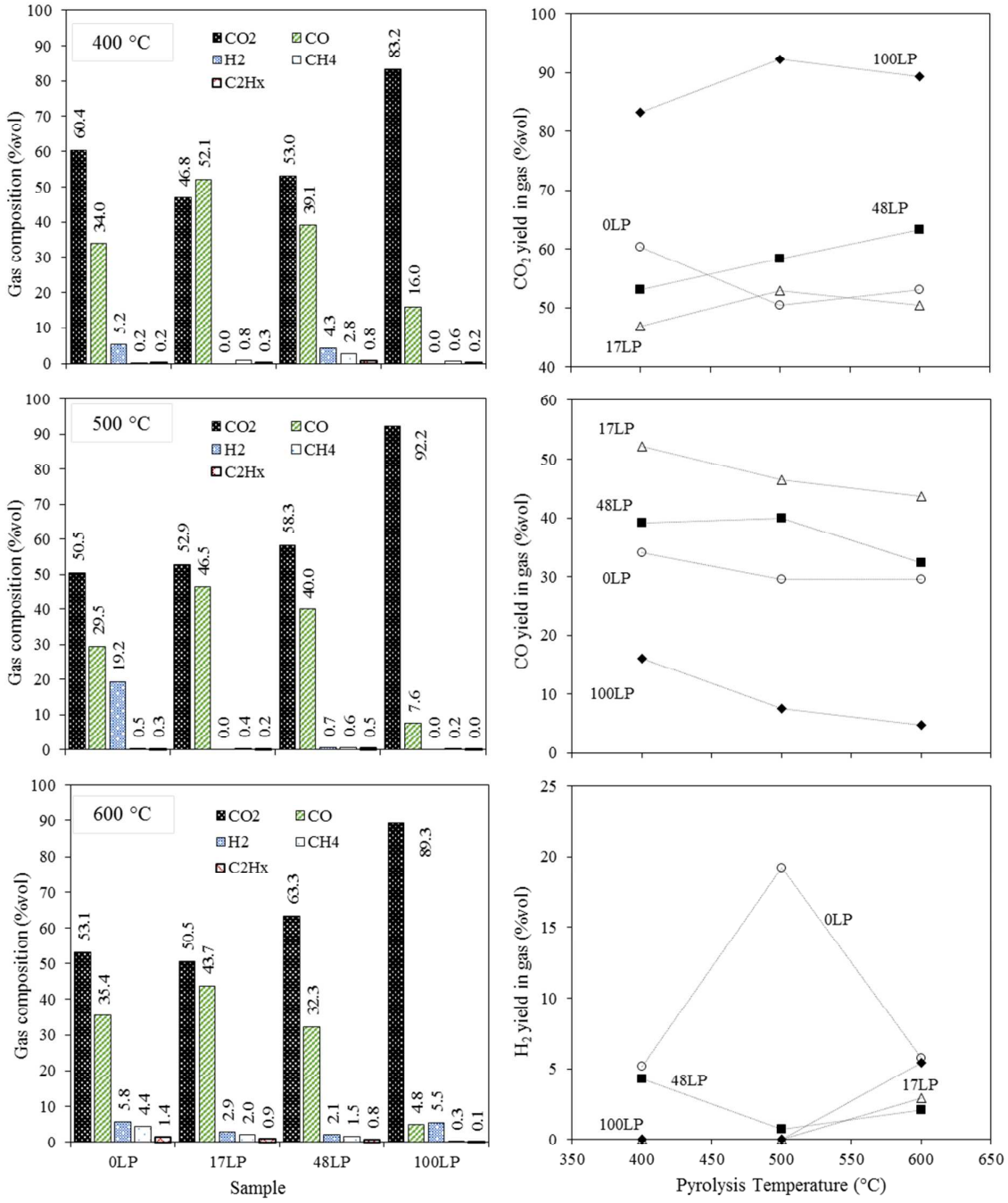


Figure 3 Pyrolysis gas composition (%vol) of different lignin-cellulose model mixtures.

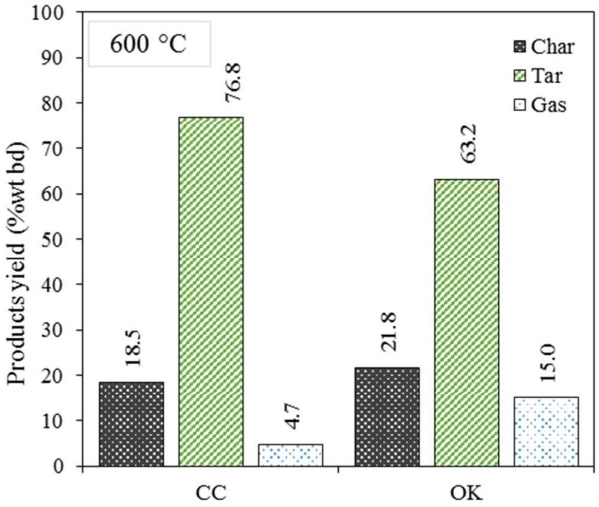


Figure 4 Comparison of the products yields (%wt, d.b.) during pyrolysis at 600 °C of woody OK and herbaceous CC waste samples.

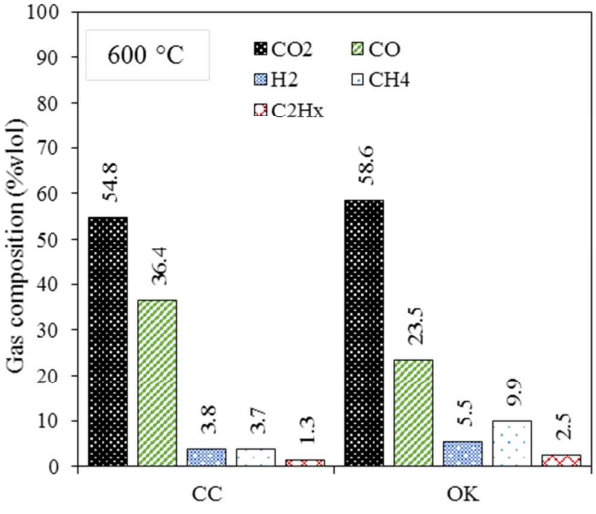


Figure 5 Comparison of the gas composition (%vol) during pyrolysis at 600 °C of woody OK and herbaceous CC, waste samples

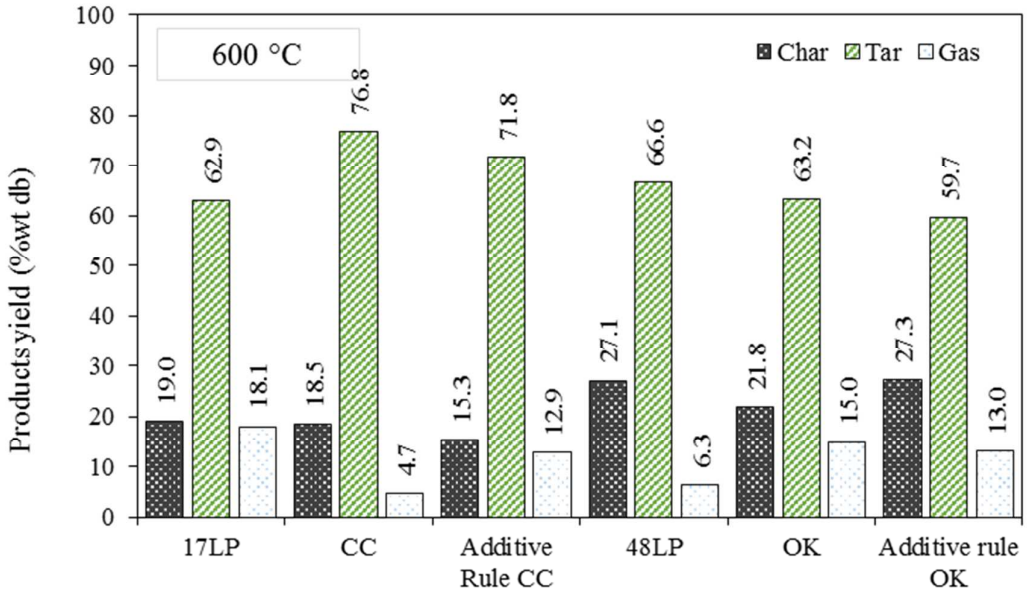


Figure 6 Comparison of the product yields (%wt, d.b.) given for both raw agro-waste and model synthetic mixtures representing their lignin and cellulose contents and deviation from the additive rule based on pure lignin and cellulose.

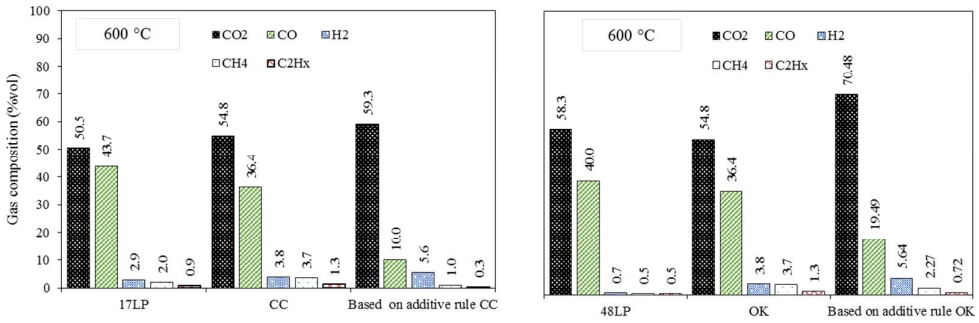


Figure 7 Pyrolysis gas composition (%vol) given for both raw agro-waste, their model synthetic mixtures carrying the same lignin content and deviation from the additive rule based on pure lignin and cellulose.

Tables

Table 1. List of experiments carried out and principal experimental conditions.

Type of Sample	Peak T (°C)	Type of Carrier Gas	Heating rate (°C/min)	Residence time (min)
0LP, 17LP, 48LP, 100LP	400 500	N_2	~150	~30
CC, OK	600			

Table 2. Proximate and ultimate analysis of raw materials. Data for LP and CM derived from suppliers.

Raw biomass specie	**Olive kernels (OK)**	**Corncobs (CC)**	**Pure Lignin (LP)**	**Pure Cellulose (CM)**
		Ultimate analysis (wt%, d.b.)		
Carbon, C	48.6	42.1	42.6	39.5
Hydrogen, H	5.7	5.5	2.6	2.6
Nitrogen, N	1.6	0.2	8.3	-
Oxygen[*]*, O*	37.0	42.14	25.5	57.9
Sulfur, S	n/a	n/a	12.6	n/a
Sodium, Na	n/a	n/a	8.7	n/a
HHV_b *(MJ/kg)*	20.5	13.2	n/a	n/a
LHV_b *(MJ/kg)*	19.2	12.0	n/a	n/a
		Proximate analysis (wt%,d.b)		
Moisture	12.3	6.0	n/a	n/a
Volatiles	79.9	71.0	n/a	n/a
Fixed C	17.2	9.6	n/a	n/a
Ash	3.6	13.3	<0.1	n/a
		Lignocellulose		
Lignin (wt%)	48	17	100	0
Hollocellulose (wt%)	52	83	0	100
Molecular Type	$CH_{1.4}O_{0.6}$	$CH_{1.5}O_{0.7}$	$CH_{0.7}O_{0.4}N_{0.2}S_{0.1}Na_{0.1}$	$CH_{0.8}O_{1.1}$

** By difference for OK and CC samples, d.b.: dry basis, n/a: not available*

Table 3 Ash elemental analysis of OK and CC.

	Ni	**Na**	**Mn**	**Mg**	**K**	**Fe**	**Cu**	**Ca**	**Al**
Corn Cobs (ppm)	*0*	*342*	*1.13*	85	137	12	4.45	258	41
Olive kernel (ppm)	*4.2*	*2130*	*12*	1000	5000	438	37	4160	760